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The Microscopic Nonequilibrium Process in Solids under Transient Heating[1]

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A brief review of studies on the dynamic process of thermal expansion since the eighties is given. A magnitude of difference of one to two orders between the results of theoretical calculations and experimental observations of the characteristic time is discussed. The nonequilibrium localized phonon gas in a "hot spot" is studied using the Boltzmann equation, leading to a soliton-like solution. It gives the way to fill the gap of the above-mentioned difference between theory and experiment. The lattice relaxation of a laser rod is developed theoretically and verified experimentally. Different expansion processes of a high-T_c superconductor below and above T_c imply the existence of some new features of excitons in the high-T_c state.

KEY WORDS: high-T_c superconductor; nonequilibrium process; thermal expansion; transient heating.

1. INTRODUCTION

The dynamic process of thermal expansion in thin foils has been studied both theoretically and experimentally at this institute since the early eighties [1–4]. But one finds that there is a difference of about one to two orders of magnitude between the calculated and the observed characteristic time of the dynamic process [3–7].

Since then, some theoretical and experimental studies have been made. Some further experiments, concerning the microscopic nonequilibrium process in solids under transient heating, either by laser or by ohmic pulse, have also been performed. In the meantime, the macroscopic theory about

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dynamic thermal expansion has been given elsewhere [8]. The experimental studies show not only the universality of the dynamic process of thermal expansion in solids, but also the possibility of improvement of material structures and properties by taking advantage of this dynamic effect.

2. A BRIEF REVIEW OF STUDIES ON THE DYNAMIC PROCESS OF THERMAL EXPANSION

The anharmonic vibration of a one-dimensional lattice can be described as [1]:

$$m\frac{du_n^2}{dt^2}=2c[(u_{n+1}-u_n)-(u_n-u_{n-1})]-3g[(u_{n+1}-u_n)^2-(u_n-u_{n-1})^2] \tag{1}$$

where m is the mass of the particle, t is time, u_n is the displacement of the nth particle, c is the stiffness of the first order, and g is the stiffness of the second order.

By analytical treatment, the exact solution of this nonlinear differential equation set is [1]

$$u_n(t)=p\left[i\left(\frac{18gu_0}{m}\right)^{1/2}\left(\frac{T}{T_0}\right)^{1/6}a^{3/2}t+\phi\right]u_0\left(\frac{T}{T_0}\right)^{1/3}\left(n^3+\frac{n}{2}\right)a^3+\frac{nc}{3g} \tag{2}$$

where a is the lattice constant, T_0 and T are temperatures, u_0 and ϕ are constants, and $p[\lambda t+\phi]$ is the Weierstrass elliptical function.

Taking statistical average, this solution yields [1]

$$\tau_N=\frac{3Ng}{4c^2}\sqrt{\frac{\pi mkT}{2}} \tag{3}$$

where k is the Boltzmann constant. Equation (3) implies that the characteristic time τ_N for the thermal expansion of the whole lattice is proportional to the length of the N-particle lattice.

The theoretical prediction of the dynamic process of thermal expansion had been verified by indirect observation through the electrical resistance measurement of a laser pulse-irradiated thin foil [4] and direct observations [5, 6]. An infrared radiation pyrometer for transient temperature measurement and a photoelectric instrument for micrometric length-change measurement were developed. After being heated by a CO_2 laser pulse 0.1 μs in duration, the transient temperature-rise history and length change due to the thermal expansion of 20 to 50 μm-thick aluminum films over a

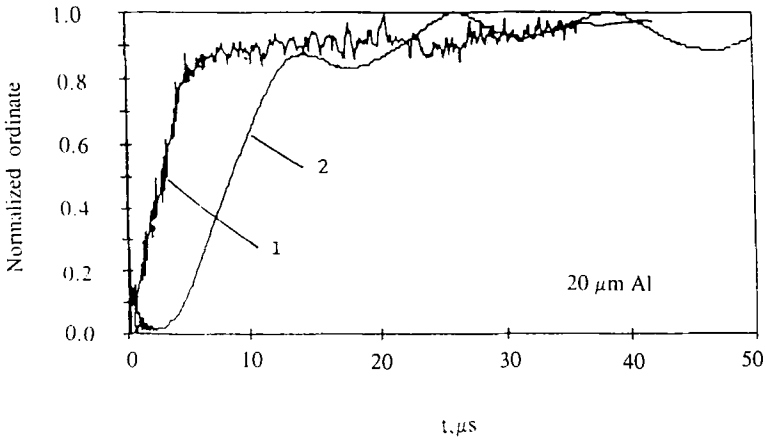

Fig. 1. Comparison of temperature rise (curve 1) and thermal-expansion (curve 2) versus time for laser pulse-heated, 20-μm-thick aluminium film [3, 5].

period of tens of microseconds were recorded. Nonsynchronous change of temperature and thermal expansion under transient heating was observed as shown in Fig. 1. Results on both conductors and insulators showed reasonable values for the time dependence of the expansion process on sample length [2].

Once the incident photons interact with electrons, the electron–electron, electron–phonon, and phonon–phonon interactions take place in the irradiated thin foil. To have an insight into the microscopic physical mechanism of the dynamic process, these interactions have been studied analytically [7]. The damping rates of the phonons in the different processes $\Gamma_p^1(\omega)$, etc., are as follows:

$$\Gamma_p^1(\omega) = 4\pi \int \frac{d\vec{k}}{(2\pi)^2} |V_q|^2 \, \delta(E_k - E_{k-q} - \omega_q)[f^0(E_{k-q}) - f^0(E_k)] \tag{4}$$

$$\Gamma_Q^1(E) = 4\pi \int \frac{d\vec{q}}{(2\pi)^2} |V_q|^2 \, \delta(E_k - E_{k-q} - \omega_q)[1 + N^0(\omega_q) - f^0(E_{k-q})] \tag{5}$$

$$\Gamma_Q^2(E) = 4\pi \int \frac{d\vec{q}}{(2\pi)^2} |V_q|^2 \, \delta(E_{k+q} - E_k - \omega_q)[N^0(\omega_q) - f^0(E_{k+q})] \tag{6}$$

$$\Gamma_P^2(\omega) = 2\pi \sum_{j_1 j_2} \int \frac{d\vec{q}_1}{(2\pi)^2} |V_3(-\vec{q}j, \vec{q}_1 j_1, \vec{q}_2 j_2)|^2 \, \delta(\omega_{jq} - \omega_{j_1 q_1} - \omega_{j_2 q_2}) \times [1 + N_{j_1}^0(\omega_1) + N_{j_2}^0(\omega_2)] \tag{7}$$

Table I. Calculated Results for the Characteristic Time of the Damping Rate and Lifetime of Different Phonon Processes

Mode	Γ_P^1	Γ_Q^1	Γ_Q^2	Γ_{P1}^2	Γ_{P2}^2
Decay rate (s^{-1})	1.20×10^{10}	1.20×10^{10}	1.76×10^{9}	3.49×10^{7}	4.40×10^{6}
Lifetime (s)	8.30×10^{-11}	8.30×10^{-11}	5.68×10^{-10}	2.87×10^{-8}	2.28×10^{-7}

where $\mathbf{k}$ is the electron wave vector, E is the electron energy, $f(E)$ is the distribution of electrons, V_q is the matrix elements of electron–phonon interaction, $N(\omega)$ is the distribution function of phonons, and V_3 is the matrix element of three-phonon interaction. It can be seen that there is still a one to two orders of magnitude difference between the characteristic time of the dynsamic process calculated (10^{-7} s is the longest lifetime ($\Gamma_{P2}^2)^{-1}$ for the three-phonon process listed in Table I [3]) and that observed (10^{-6}–10^{-5} s) [3]. In an attempt to explain this difference, both microscopic and macroscopic theoretical treatments have been made.

3. NONEQUILIBRIUM LOCALIZED PHONON GAS IN A "HOT SPOT" [9]

The nonequilibrium thermal process of localized phonons in a "hot spot", in which the phonon mean free path is greatly reduced by phonon-phonon scattering, can be described by the nonlinear Boltzmann equation [10]:

$$\left[\frac{\partial}{\partial t}+\vec{v}_j\cdot\nabla\right] n_j(\vec{k},\vec{r}t)$$
$$= -(4\omega_j)^{-1}\left[\prod_{jj,k}^{>}(\omega_j,\vec{r}t)\cdot n_j(\vec{k},\vec{r}t)-\prod_{jj,k}^{<}(\omega_j,\vec{r}t)(1+n_j(\vec{k},\vec{r}t))\right] \quad (8)$$

where $n_j(\mathbf{k},\mathbf{r}t)$ is the distribution function of phonons at position $\mathbf{r}$ and time t with wave vector $\mathbf{k}$, v_j is the phonon velocity, and ω_j is the phonon frequency. $\prod_{jj,\mathbf{k}}^{>}$ and $\prod_{jj,\mathbf{k}}^{<}$ are self-energy functions of phonons. If only the three-phonon process is considered, the right side of Eq. (8) can be expressed as [11]

$$-\tfrac{1}{2}\hbar\pi\sum_{jj_1j_2}|U^{(3)}_{jj_1j_2}|^2(2\omega_j\cdot2\omega_{j_1}\cdot2\omega_{j_2})^{-1}\cdot\{\delta(\omega_j-\omega_{j_1}-\omega_{j_2})[(1+n_{j_1})(1+n_{j_2})n_j$$
$$-n_{j_1}n_{j_2}(1+n_j)]+2\delta(\omega_j-\omega_{j_1}+\omega_{j_2})$$
$$\times[(1+n_{j_1})n_{j_2}n_j-n_{j_1}(1+n_{j_2})(1+n_j)]\} \quad (9)$$

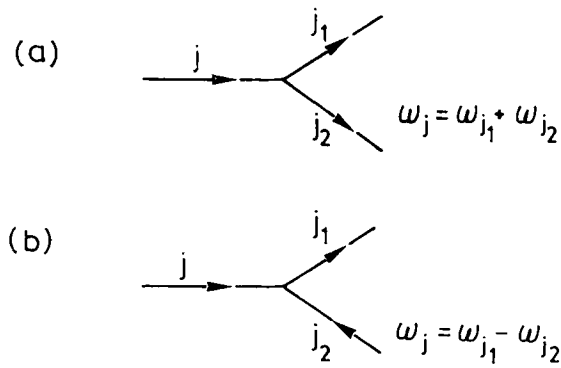

Fig. 2. Two cases of the three-phonon process.

where $U^{(3)}_{jj_1j_2}$ is the nonlinear coefficient of lattice and h is the Planck constant. There are two cases in the three-phonon process (Fig. 2).

For simplicity, Eq. (9) can be transformed into a one-dimensional form:

$$\left(\frac{\partial}{\partial t} + v_s \frac{\partial}{\partial x}\right) n_j = -a n_j^2 - b n_j + b n_j^{\mathrm{E}} \tag{10}$$

where $a = \pi h\, |U^{(3)}_{jj_1j_2}|^2$, $b = (1/\tau_{\mathrm{N}} + 1/\tau_{\mathrm{U}})$, and τ_{N} and τ_{U} are relaxation times [10] for normal and Umklapp processes, respectively, and $n_j^{\mathrm{E}} = 1/\{\exp[\beta(h\omega_j - v_j \cdot P)] - 1\}$ is the local equilibrium distribution function of phonons.

According to the Taniuti method [12], the solution of Eq. (10) is the expansion of steady and homogeneous solution n_j^d in the form of

$$n_j = \bar{n}_j^d + \sum_{\alpha=1}^{\infty} \varepsilon^{\alpha} n_j^{(\alpha)}(\vec{k}, xt) \tag{11}$$

where ε is a small parameter and

$$n_j^{(\alpha)}(\vec{k}, xt) = \sum_{l}^{\infty} n_{jl}^{(\alpha)}(\xi, \tau)\, e^{il(kx - \omega t)} \tag{12}$$

by definition $\xi = \varepsilon(x - v_s t)$, $\tau = \varepsilon^2 t$, and $v_s = \partial\omega/\partial k$ is the group velocity of the second sound. Retaining the first major term and its conjugate term, the solution of Eq. (10) is then obtained:

$$n_j(\vec{k}, xt) = \bar{n}_j^d(\vec{k}) + \varepsilon[n_{j_1}^{(1)}(\xi, \tau)\, e^{i(kx - \omega t)} + c.c] + O(\varepsilon^2) \tag{13}$$

where $c.c$ is the conjugation symbol, and $n_{j_1}^{(1)}(\xi, \tau) = \phi^{(1)}(\xi, \tau)$, $n_{j-1}^{(1)}(\xi, \tau) = [\phi^{(1)}(\xi, \tau)]^*$, while $\phi^{(1)}(\xi, \tau)$ satisfies the following nonlinear Schrödinger equation:

$$i\phi_{\tau}^{(1)}(\xi, \tau) + \beta\phi_{\xi\xi}^{(1)}(\xi, \tau) + \rho\, |\phi^{(1)}|^2\, \phi^{(1)}(\xi, \tau) = 0 \tag{14}$$

where $\rho = -(n_s + b/2a)^{-1}$, $\beta = 1/2(\partial v_s/\partial k)$, and let γ be constant, thus the standard solution of Eq. (14) is

$$\phi^{(1)}(\xi, \tau) = \left(\frac{-2\gamma}{\rho}\right)^{1/2} \operatorname{sech}\left(\left(-\frac{\gamma}{\beta}\right)^{1/2} \xi\right) \exp(-i\gamma\tau) \tag{15}$$

this is a wave-packet form soliton-like solution. The moving velocity v_s of the soliton-like wave-packet is about 10^3 m · s^{-1} given in Ref. 13, and the lifetime of the long-lived tail of the phonons emitted from the "hot spot" will be 10 mm/10^3 m · s^{-1} = 10 μs for a 10-mm sample. Consequently, the order of magnitude of the time calculated is in fairly good agreement with the experimental value [13].

The schematic illustration of the soliton-like wave-packet of phonon distribution in the "hot spot" is shown in Fig. 3a. Comparing it with the case of a laser pulse-irradiated thin foil of length $l = 10$ mm, once the "hot spot" is formed at any point x along the foil, the soliton-like wave-packet $\phi_{j-1}^{(1)}$ will move to the left and the other $\phi_{j_1}^{(1)}$ move to the right. Passing

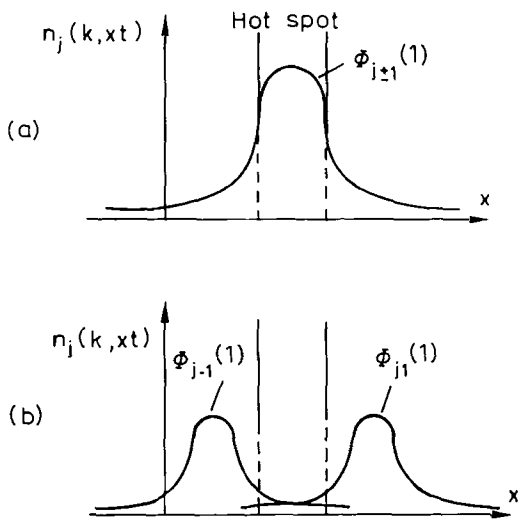

Fig. 3. (a) Phonon distribution in the "hot spot"; (b) extinction of the hot spot.

through a path of length x to a fixed point $x=0$, the packet $\phi_{j-1}^{(1)}$ will be reflected to the right along l to the free end of the foil, while the other packet $\phi_{j_1}^{(1)}$ travels over $l-x$ to the free end (Fig. 3b). The total length traveled by the two wave-packets is $x+l+(l-x)=2l$. Since the two packets starts their travel at the same time, the characteristic time will be $1/l\int_0^l [(x+l/v-l-x/v)+l-x/v]\,dx=3/2l/v=15\ \mu$s. This is also in fairly good agreement with the experimentally observed values [1–6], or in other words, the characteristic time for dynamic thermal expansion is proportional to the length of the sample and can be calculated quantitatively.

In addition, it is known from solid-state physics [14] that thermal expansion of a substance is proportional to the average thermal vibration energy in it, thus it can be said that the dynamic thermal expansion is also proportional to the phonon energy agitated by the laser pulse. Consequently, the time-dependent microscopic phonon distribution gives rise to the macroscopic time process for thermal expansion.

4. LATTICE RELAXATION OF A LASER ROD

All the samples studied in this laboratory on dynamic thermal expansion are opaque materials, which cannot be irradiated within the bulk. Next, we consider the case of a transparent material, such as the Nd glass rod in a laser equipment. The Hamiltonian can be written as

$$H=H_e+H_{el}+H_l \tag{16}$$

where H_e, H_{el}, and H_l are Hamiltonians of electrons, electron-phonon interaction, and the lattice, respectively.

The equilibrium position of any atom at i electric state Q_{is} is the sum of its equilibrium position in the ground state Q_s and the lattice relaxation Δ_{is} [15, 16]. Next, the lattice relaxation and multiphonon nonradiative transition [17] are discussed. The transition matrix element is [15, 16]

$$\langle in'|\,H\,|jn\rangle=\int \varphi_i(x,Q)\,x_{in'}(Q)\,H\varphi_j(x,Q)\,x_{jn}(Q)\,dx\,dQ \tag{17}$$

By adiabatic approximation, it becomes

$$\langle in'|\,H\,|jn\rangle=\int x_{in'}(Q)\left\{-\frac{h^2}{2}\sum_s\int \varphi_i(x,Q)\frac{\partial^2}{\partial Q_s^2}\varphi_j(x,Q)\,dx\right.$$
$$\left.-h^2\sum_s\left[\int \varphi_i(x,Q)\frac{\partial}{\partial Q_s}\varphi_j(x,Q)\,dx\right]\frac{\partial}{\partial Q_s}\right\}x_{jn}(Q)\,dQ \tag{18}$$

while the nonradiative transition probability takes the form [15]

$$W = \frac{2\pi}{\hbar} \mathrm{Av}_n \sum_{n'} |\langle in' | H | jn \rangle|^2 \delta(E_{in'} - E_{jn}) \tag{19}$$

where Av_n is the statistical average of the thermal distribution for different phonon states n under certain electric states.

To generate a laser pulse, the Nd glass rod must be excited by Xe light. After the excitation but before the emission of the laser pulse, the multiphonon nonradiative transition plays an important role, and the lattice temperature goes up with the lattice expansion. Once the laser pulse emits, together with electron-level transitions, the lattice relaxation comes into action and causes a small amount of lattice contraction superposing on the normal dynamic thermal expansion. To check these assumptions,

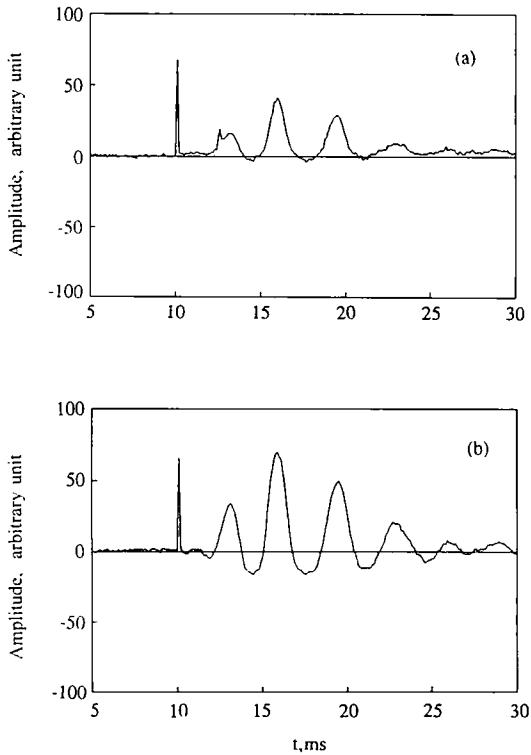

Fig. 4. Length change versus time for a Nd glass laser rod: (a) with laser pulse emission; (b) without laser pulse emission.

some experiments were conducted [18]. The length change processes of the laser rod excited by Xe light, with and without laser pulse emission are shown in Fig. 4.

It can be seen from Fig. 4 that (a) the amplitude of the dynamic length change of the rod is much larger than that of the steady-state change, shown by the portion after oscillation—the dynamic length change will cause much stronger thermal stress than that predicted by the elastic theory; (b) the characteristic time of thermal expansion in the case with the laser pulse emission is about 200 μs longer than that without the emission; and (c) the amplitude of the former case is smaller than the latter.

It should be noted that the shape of the curve for a transparent material is much different from that for an opaque material.

5. DIFFERENT EXPANSION PROCESS FOR A HIGH-T_c SUPERCONDUCTOR BELOW AND ABOVE THE T_c TEMPERATURE [19]

It is known that the steady-state thermal expansion of high-T_c superconducting materials makes almost no difference below and above the superconducting transition temperature T_c [20] as shown in Fig. 5. One almost cannot find the evident transition point on the temperature-dependent curve of thermal expansion in the vicinity of the temperature range corresponding to the transition temperature T_c of electric conductivity.

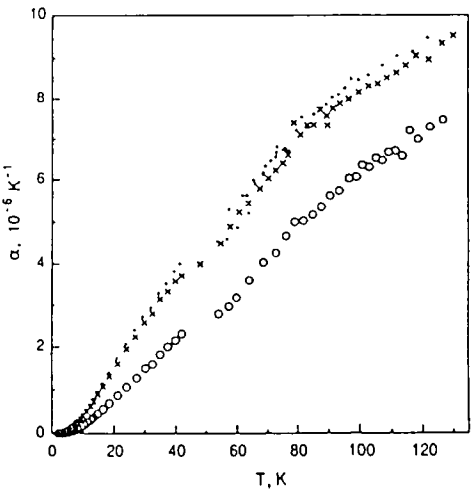

Fig. 5. $\alpha(T)$ below 130 K for BPSC6 (●), BSC2 (×), and BPSC8 (○) [20].

Some recent observations on the dynamic process of the thermal expansion of high-T_c superconducting material $Bi_2Sr_2Ca_2Cu_3O_{10}$ (BSCCO) thin foils have been made in this laboratory [19]. The BSCCO samples were prepared at this institute by the High-T_c Group. The sample size is 25 mm in length, 5 mm in width, and 300 μm in thickness, and the transition temperature T_c is 105 K.

The dynamic process of thermal expansion of these samples was observed essentially in the same manner as before [2, 5], but the lowest temperature was near 80 K. Figure 6 shows the typical curves of length change versus time for the same sample under transient laser pulse (0.1 μs) heating at different temperatures. It can be seen that for the same sample under same heating energy, the amplitude at 83 K ($<T_c$) (Fig. 6a) is almost one order of magnitude higher than that at 113 K ($>T_c$) (Fig. 6b). This phenomenon was repeatable many times [19].

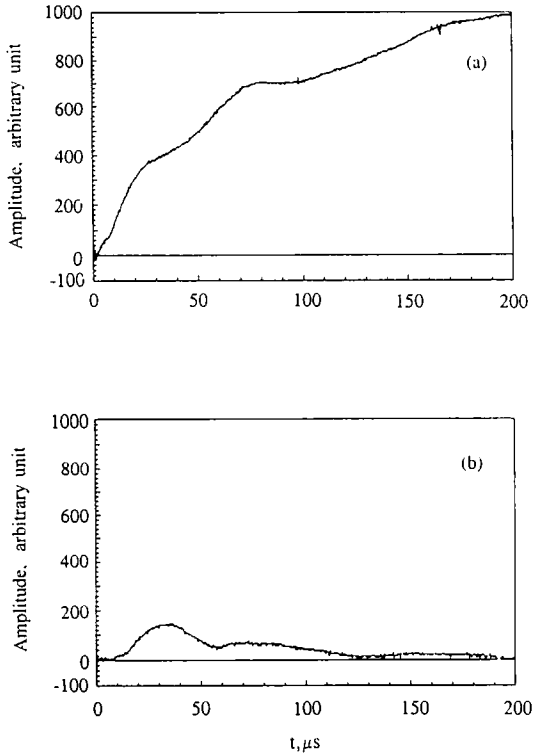

Fig. 6. Lenght change versus time for the same thin foil sample of a high-T_c superconductor $Bi_2Sr_2Ca_2Cu_3O_{10}$ under laser pulse heating at different temperatures: (a) at 83 K and (b) at 133 K ($T_c = 105$ K).

It is believed that as long as BSCCO is in the normal state above T_c, there are only a few free electrons participating in the interaction with incident photons together with some localized electrons. That is only a small amount of energy can be imparted to the lattice to cause expansion, while in the superconducting state below T_c, a great number of carriers will be excited by the incident photons and a large amount of energy can be absorbed. The carriers are believed to be a new kind of excitons to be determined. Once the photon energy is brought in, the excitons are excited to a higher temperature than the lattice and then transfer their energy to the phonons through a series of particle–particle interactions as described in the preceding sections. Consequently, the amplitude of the length change of BSCCO below T_c is much higher than that above T_c.

6. CONCLUDING REMARK

A series of theoretical and experimental studies on the dynamic process of thermal expansion of solids shows the universality of dynamic phenomenon, and the characteristic time of the expansion process calculated is in fairly good agreement with the observed result. The results on lattice relaxation of a laser rod and a high-T_c superconductor are interesting and worthy of further studies.

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